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PATENT **13311US**

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AUG 0 5 2004
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Starz, et al.	Examiner:	Wills, Monique M.
Serial No.:	09/915,764	Group Art Unit:	1746
Filed:	July 27, 2001		
For:	Ink for the production of membrane electrode units for PEM fuel cells		
Customer No.:	23719 PATENT TRADEMARK OFFICE		

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August 5, 2004

Commissioner for Patents
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S I R:

Applicants enclose certified English translation of the priority document of German Patent Application No. 100 37 074.8, which was filed July 29, 2000. The present application properly claims priority to German Patent Application No. 10 037074.8. Applicants have previously filed a certified priority document and the Examiner has acknowledged priority under 35 U.S.C. § 119. Applicants respectfully submit that the present application is entitled to the benefit of the earlier filing date of July 29, 2000.

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UNITED STATES PATENT AND TRADEMARK OFFICE

I, Susan ANTHONY BA, ACIS,

Director of RWS Group Ltd, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.

2. That the translator responsible for the attached translation is well acquainted with the German and English languages.

3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in Germany on 29 July 2000 under the number 100 37 074.8 and the official certificate attached hereto.

4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group Ltd

The 23rd day of July 2004

FEDERAL REPUBLIC OF GERMANY

[Eagle crest]

Priority Certificate

for the filing of a Patent Application

File Reference: 100 37 074.8

Filing date: 29 July 2000

Applicant/Proprietor: Umicore AG & Co KG, 63457 Hanau/DE

(formerly: dmc2 Degussa Metals Catalysts Cerdec AG, 60287 Frankfurt/DE)

Title: Ink for producing membrane-electrode units for PEM fuel cells

IPC: H 01 M 8/02

The attached documents are a correct and accurate reproduction of the original submission for this Application.

Munich, 1 July 2004

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Ink for producing membrane-electrode units for PEM fuel cells

Description

The present invention relates to an ink for producing membrane-electrode units for fuel cells, in particular for polymer electrolyte membrane fuel cells (PEM fuel cells). A novel, water-containing catalyst ink for producing membranes coated with catalyst, electrodes and membrane-electrode units (MEE) is described.

Fuel cells convert a fuel and an oxidant at separate locations at two electrodes into electric power, heat and water. The fuel employed can be hydrogen or a hydrogen-rich gas, while the oxidant employed can be oxygen or air. The energy conversion process in the fuel cell has a particularly high efficiency. For this reason, fuel cells combined with electric motors are becoming increasingly important as alternatives to conventional internal combustion engines. Owing to its compact construction, its power density and its high efficiency, the PEM fuel cell is particularly suitable for use as energy transformer in motor vehicles.

The PEM fuel cell comprises a stack of membrane-electrode units (MEE) between which bipolar plates for introduction of gas and output of electric power are arranged. A membrane-electrode unit comprises a solid polymer electrolyte membrane which is provided on both sides with catalyst-containing reaction layers. One of the reaction layers is configured as anode for the oxidation of hydrogen and the second reaction layer is configured as cathode for the reduction of oxygen. Gas distributor structures made of carbon fiber paper or carbon felt, which allow good access of the reaction gases to the electrodes and make it possible for the electric current from the cell to be taken off readily, are applied to these reaction layers. Anode and cathode

comprise electrocatalysts which catalyze the respective reaction (oxidation of hydrogen at the anode or reduction of oxygen at the cathode). As catalytically active components, preference is given to using the metals of the platinum group of the Periodic Table of the Elements. In the majority of cases, supported catalysts in which the catalytically active platinum group metals have been applied in finely divided form to the surface of a conductive support material are used.

The polymer electrolyte membrane comprises proton-conducting polymer materials. These materials will hereinafter also be referred to as ionomers for short. Preference is given to using a tetrafluoroethylene-fluorovinyl ether copolymer having acid functions, in particular sulfonic acid groups. Such materials are marketed, for example, under the trade names Nafion® (E.I. du Pont) or Flemion® (Asahi Glass Co.). However, it is also possible to use other, in particular fluorine-free, ionomer materials such as sulfonated polyether ketones or aryl ketones or polybenzimidazoles. Furthermore, ceramic membranes and other high-temperature materials can also be used.

The performance date of a fuel cell depend decisively on the quality of the catalyst layers applied to the polymer electrolyte membrane. These layers are mostly highly porous and usually comprise an ionomer and a finely divided electrocatalyst dispersed therein. Together with the polymer electrolyte membrane, three-phase interfaces are formed in these layers, and at these interfaces the ionomer is in direct contact with the electrocatalyst and the gases brought to the catalyst particles via the pore system (hydrogen at the anode, air at the cathode).

To produce the catalyst layers, ionomer, electrocatalyst, solvent and, if appropriate, other

additives are carefully mixed with one another to form an ink or paste. To form the catalyst layer, the ink is applied by brushing, rolling, spraying, doctor blade coating or printing either to the gas distributor structure (e.g. carbon fiber felt or carbon fiber paper) or directly to the polymer membrane, dried and, if appropriate, after-treated. When the ionomer membrane is coated with a catalyst layer, the uncatalyzed distributor structures are subsequently joined on the anode and cathode sides to the membrane so as to give the membrane-electrode unit (MEE). If the gas distributors are coated with a catalyst layer, these catalyzed gas distributor structures are placed on both sides of the ionomer membrane and subsequently pressed together with this, likewise giving an MEE.

Various ink compositions are known from the patent literature. Thus, an ink comprising, based on the total weight of the ink, 3.1% by weight of a Pt/C catalyst (30% by weight of platinum on carbon black), 30.9% by weight of a 5% strength ionomer solution in a mixture of 90 parts of isopropanol and 10 parts of water, 37.2% by weight of glycerol, 24.8% by weight of water, 2.5% by weight of tetrabutylammonium hydroxide and 1.5% by weight of pore former is used in DE 196 11 510 A1 for producing membrane electrode units for fuel cells. The total water content of the ink is 27.7% by weight. Owing to the high isopropanol content of this ink, appropriate precautions have to be taken during manufacture to prevent unintended ignition of the catalyst. In addition, it has been found that, owing to the low boiling point of isopropanol, the ink can be processed by means of screen printing only during a very short time, viz. the "screen processing life" in screen printing is unsatisfactory. Furthermore, the glycerol present in the ink results in the membrane-electrode unit (MEE) requiring a very long activation and running-in time before acceptable electrical values are obtained.

Furthermore, printing inks which use alcohols having a boiling point above 100°C (US 5,871,552) or alkylene carbonates such as propylene carbonate (US 5,869,416) as solvents are known. Furthermore, DE 198 12 592 A1 describes an ink comprising two immiscible organic solvents A and B. As solvent A, use is made of monohydric or polyhydric alcohols, glycols, glycol ether alcohols, glycol ethers and mixtures thereof. Solvents B are nonpolar hydrocarbons or weakly polar solvents. A typical ink of this type (cf. example 1 of DE 198 12 592 A1) comprises 13.4% by weight of a Pt/C electrocatalyst, 67% by weight of a 6.7% strength solution of an ionomer (Nafion) in propylene glycol (solvent A), 17.9% by weight of methyl dodecanoate (solvent B) and 1.7% by weight of aqueous sodium hydroxide solution (10% strength). All these catalyst inks do not contain any water but instead contain only organic solvents. Owing to the high solvent content, they are prone to ignition. The considerable emissions of organic compounds (solvents are "volatile organic compounds" = VOC) present a problem in respect of occupational hygiene and environmental protection, particularly in the mass production of components for fuel cells.

For this reason, inks whose major solvent is water have become known. Thus, EP 0309337 A1 describes a water-containing electrode ink comprising alcohols and water. The ionomer is in this case dissolved in a mixture of water and ethanol or isopropanol, with the water content being greater than 86% by volume.

EP 0 026 979 A2 describes a water-based ink which, however, does not contain an ionomer but instead hydrophobic Teflon. This ink is therefore unsuitable for electrodes and MEEs used in PEM fuel cells.

EP 0 731 520 A1 describes an ink which comprises a

catalyst, ionomer and solvent and in which water is used as solvent. Apart from the ionomer, this ink contains no further organic components. Testing of this ink by the present inventers indicated that it leads to electrode layers which do not adhere well to the polymer membrane. As a result, the electric power of the MEEs produced using this ink is unsatisfactory. Likewise, screen printing using this ink shows that it thickens very quickly and thus has an unsatisfactory processing life in screen printing.

It is therefore an object of the present invention to provide a water-based catalyst ink which does not contain any toxic and/or highly flammable solvents and, in addition, overcomes the disadvantages of the water-based catalyst ink described in EP 0 731 520 A1 (poor adhesion, poor electric power, short processing life). The use of this new ink should guarantee high production safety in the field of occupational hygiene and environmental protection and be particularly suitable for screen printing.

This object is achieved by an ink for producing electrodes for PEM fuel cells which comprises a catalyst material, an ionomer, water and an organic solvent (cosolvent). The ink has the feature that the organic solvent is at least one compound from the group consisting of linear dialcohols having a flash point above 100°C and is present in the ink in a concentration of from 1 to 50% by weight, based on the weight of water.

For the purposes of the present invention, linear dialcohols are dihydric alcohols which have two hydroxyl groups in their linear, chain-like molecular framework. The hydroxyl groups do not have to be adjacent to one another (i.e. vicinal). The chain framework can comprise aliphatic CH_2 groups, if desired with oxygen atoms between them (ether bridges).

Possible organic solvents for the catalyst inks of the invention are, for example:

ethylene glycol (1,2-ethanediol)	flash point 111°C
diethylene glycol	flash point 140°C
1,2-propylene glycol (1,2-propanediol)	flash point 101°C
1,3-propylene glycol (1,3-propanediol)	flash point 131°C
dipropylene glycol	flash point 118°C
1,3-butanediol	flash point 109°C
1,4-butanediol	flash point 130°C

and further compounds of this group. The flash point is determined in a closed crucible by the Pensky-Martens method in accordance with the European Standard EN 22719. The data have been taken from the CHEMSAFE databank (Dechema e.V.) and represent "recommended values".

The solvents are generally soluble in water or miscible with water, and are largely unproblematical in hydrological and toxicological terms. Thus, ethylene glycol, the propylene glycols and butylene glycols are not subject to compulsory labeling. Their use in industrial drying plants thus presents no problems.

It has been found that an ink comprising substantially water as solvent displays surprisingly good adhesion to the polymer membrane when it further comprises from 1 to 50% by weight, preferably from 5 to 25% by weight, (based on the water content of the ink) of a compound from the group consisting of linear dialcohols having flash points above 100°C as additional solvent. In addition, this ink displays very good processing lives in screen printing and also good electric power values in the PEM fuel cell. The linear dialcohols obviously result in intimate contact of the catalyst layer with the ionomer membrane and thus result in good adhesion

and electric power.

Since the main component in the ink of the invention is still water (proportion of solvent is preferably 5 - 25% by weight, based on the water content) and the linear dialcohols have a flash point of above 100°C, the problems of high flammability and the low ignition temperatures known for the conventional, solvent-containing inks do not occur.

A high degree of production safety is thus achieved in the processing of these inks. In addition, when used in screen printing, they make it possible to achieve a long processing life which is significantly superior to that of pure water pastes (according to EP 0 731 520 A1).

To produce the paste, ink or preparation of the invention, the components

- EM-containing supported catalyst (e.g. 40% Pt on conductive carbon black)
- ionomer solution in aqueous form (e.g. aqueous Nafion solution)
- deionized water
- additional, organic solvent (cosolvent)

are weighed into a suitable container and dispersed. As dispersing equipment, use is made of apparatuses for generating high shear forces (high-speed mixers, roll mills etc.).

The ink of the invention is applied directly to a polymer electrolyte membrane. However, it can also be applied to the gas distributor structure (e.g. carbon fiber paper or carbon fiber fabric). Various coating methods such as spraying, screen printing, stenciling or offset printing can be used for this purpose. Suitable coating methods are described in US 5,861,222.

The polymer electrolyte membrane consists of a proton-conducting film. Such material is marketed as film for example under the trade name Nafion® by E.I. DuPont. Furthermore, the ionomer can also be obtained in aqueous solution with low molecular weight, aliphatic alcohols (Fluka, Buchs; Aldrich, Steinheim). Aqueous solutions of the ionomer in relatively high concentrations (10%, 20%) can be prepared from these. However, it is in principle also possible to use all other, in particular fluorine-free ionomer materials such as sulfonated polyether ketones, aryl ketones or polybenzimidazoles as film or as solution.

As catalysts, it is possible to use all electrocatalysts known in the field of fuel cells. In the case of supported catalysts, a finely divided, electrically conductive carbon is used as support. Preference is given to using carbon black, graphite or activated carbon. As catalytically active component, use is made of the platinum group metals, e.g. platinum, palladium, ruthenium and rhodium or alloys thereof. The catalytically active metals can further comprise additional alloying constituents such as cobalt, chromium, tungsten, molybdenum, vanadium, iron, copper, nickel, etc. Depending on the layer thickness of the electrode, area concentrations of metal in the reaction layers of from 0.01 to 5 mg of noble metal/cm^2 are possible. The reaction layers can be produced using platinum electrocatalysts on carbon black (Pt/C) containing from 5 to 80% by weight of platinum or else unsupported catalysts such as platinum black or platinum powder having a high surface area. Suitable electrocatalysts are described in EP 0 743 092 and DE 44 43 701.

Apart from these components, the ink of the invention can further comprise additives such as wetting agents, leveling agents, antifoams, pore formers, stabilizers,

pH modifiers and other substances.

To determine the electric power, the membrane-electrode unit produced using the catalyst inks is examined in a PEM full cell test. Here, the PEM cell is operated using hydrogen and air at atmospheric pressure (about 1 bar) and the performance curve (voltage/current density curve) is determined. From this performance curve, the cell voltage achieved at a current density of 500 mA/cm^2 is determined as a measure of the electrocatalytic performance of the cell. To allow better comparability of the ink systems, the catalyst loading is kept constant (total loading about 0.2 - 0.6 mg Pt/cm^2).

The ink of the invention can be processed readily in various coating processes and displays very good adhesion to all customary polymer electrolyte membranes (ionomer films such as Nafion® or Flemion®). The membrane-electrode units give a high electric power in the PEM fuel cell. The electric power is typically far above that obtained using a pure water paste.

The following examples illustrate the invention. Figure 1 shows the dependence of the cell voltage on the current density for the membrane-electrode units produced in comparative example 1 und example 1 using the ink of the invention.

<u>Comparative example 1:</u> (Ink according to EP 0 731 520 A1)

The following components were weighed out and homogenized by means of a dispersing apparatus:

15.0 g	of supported Pt catalyst (40% Pt/C, from Degussa-Hüls)
50.0 g	of Nafion® solution (10% in water)
35.0 g	of water (deionized)

100.0 g

The weight ratio of catalyst/Nafion® in this ink was 3:1. The ink was applied by screen printing to the anode and cathode sides of an ionomer membrane Nafion® 112 (from DuPont) in the form of a square having an edge length of 7,1 cm (active cell area: 50 cm^2) and subsequently dried at 80°C. The adhesion of the catalyst layers to the ionomer membrane were found to be unsatisfactory; in particular, detachment of the electrode layers in some places occurred after drying and subsequent irrigation of the ionomer membrane.

After drying and irrigation, the MEE was placed between two gas distributor substrates (TORAY carbon paper, thickness 225 µm) and measured in a PEM full cell operated using hydrogen/air. At a current density of 500 mA/cm^2, a cell voltage of 560 mV was measured (cf. fig. 1, type A). The total Pt loading (anode and cathode) was 0.6 mg of Pt/cm^2.

Example 1:

Comparative example 1 was altered by reducing the amount of water to 27 g and, according to the invention, making up the difference with 8 g of dipropylene glycol:

15.0 g	of supported Pt catalyst (40% Pt/C, from Degussa-Hüls)
50.0 g	of Nafion® solution (10% in water)
27.0 g	of water (deionized)
8.0 g	of dipropylene gycol
100.0 g	

The weight ratio of catalyst/Nafion® was 3:1. The proportion of dipropylene glycol was 11% by weight (based on the total water content). The ink was, as

described in comparative example 1, applied to the anode and cathode sides of the ionomer membrane Nafion® 112. The adhesion of the electrode layers to the membrane after drying and irrigation was very good, and no detachment of the layers was observed. The total Pt loading was 0.6 mg of Pt/cm^2. The MEE produced in this way was measured in an PEM full cell test. At a current density of 500 mA/cm^2, a cell voltage of 634 mV was measured. This value is about 70 mV above the cell voltage of comparative example 1 (cf. figure 1). The ink according to the invention is thus significantly superior to the ink of comparative example 1.

Example 2:

The following components are weighed out and homogenized:

15.0 g	of supported PtRu catalyst (40% Pt/C: 26.4% Pt, 13,6% Ru; catalyst corresponding to US 6,007,934)
60.0 g	of Nafion® solution (10% in water)
15.0 g	of water (deionized)
10.0 g	of ethylene gycol
100.0 g	

The weight ratio of catalyst/Nafion® was 2.5:1. The proportion of ethylene glycol was 14.5% by weight (based on the total water content). The ink was applied to the anode side of an ionomer membrane (Nafion® 112, from DuPont) and subsequently dried at 80°C. The ink according to the invention from example 1 was subsequently applied to the reverse side of the membrane (cathode side) and once again dried. After drying, the MEE was irrigated and subsequently placed in a moist condition between two gas distributor substrates. The adhesion of the catalyst layers to the membrane was very good. Measurement was carried out in a PEM full cell operated using hydrogen/air. At

500 mA/cm^2, a cell voltage of 620 mV was measured. Even when operated using reformer gas (gas composition: 60% by volume of hydrogen, 25% by volume of carbon dioxide, 15% by volume of nitrogen, 40 ppm of carbon monoxide), the MEE gave very good performance, viz. 600 mV at 500 mA/cm^2.

Example 3:

A further ink having the following composition was prepared:

15.0 g	of supported Pt catalyst (40% Pt/C, from Degussa-Hüls)
50.0 g	of Nafion® solution (10% in water)
20.0 g	of water (deionized)
15.0 g	of diethylene gycol
100.0 g	

The weight ratio of catalyst/Nafion® was 3:1. The proportion of diethylene glycol was 23% by weight (based on the total water content). The ink was applied to front and reverse sides of an ionomer membrane (thickness: 30 μm). The adhesion of the catalyst layers after drying and irrigation was very good. The power in the PEM full cell operated using hydrogen/air was 650 mV at a current density of 500 mA/cm^2.

Example 4:

The ink of example 2 was applied by means of screen printing to a gas distributor structure provided with a carbon black equalizing layer and subsequently dried at 80°C. The loading of the anode gas distributor produced in this way was 0.3 mg of Pt/cm^2 and 0.15 mg of Ru/cm^2. The active cell area was 50 cm^2. In a second step, the ink of example 1 was applied to a gas distributor structure, once again by means of screen printing, and

dried. The cathode gas distributor produced in this was had a loading of 0.4 mg of Pt/cm^2. To produce a membrane-electrode unit, a dry ionomer membrane (Nafion 112, from DuPont) was inserted between anode and cathode gas distributors and pressed together at 135°C under a pressure of 7 kN. The assembly produced in this way was installed in a PEM fuel cell and measured in operation using reformer/air (for gas composition, see example 2). The cell voltage was 630 mV at a current density of 500 mA/cm^2.

Claims

1. An ink for producing membrane-electrode units for PEM fuel cells which comprises a catalyst material, an ionomer, water and an organic solvent, wherein the organic solvent is at least one compound from the group consisting of linear dialcohols having a flash point above 100°C and is present in the ink in a concentration of from 1 to 50% by weight, based on the weight of water.

2. The ink as claimed in claim 1, wherein the organic solvent is present in the ink in a concentration of from 5 to 25% by weight, based on the weight of water.

3. The ink as claimed in claim 1, wherein the organic solvent present in the ink is ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butanediol or a mixture thereof.

4. The use of the ink as claimed in any of claims 1 to 3 for producing catalyst-coated membranes for PEM fuel cells.

5. The use of the ink as claimed in any of claims 1 to 3 for producing membrane-electrode units for PEM fuel cells.

6. The use of the ink as claimed in any of claims 1 to 3 for producing catalyst-coated gas distributor substrates for PEM fuel cells.

Abstract

The invention relates to an ink for producing membrane-electrode units for PEM fuel cells which comprises a catalyst material, an ionomer, water and an organic solvent. The ink has the feature that the organic solvent is at least one compound from the group consisting of linear dialcohols having a flash point above 100°C and is present in the ink in a concentration of from 1 to 50% by weight, based on the weight of water.

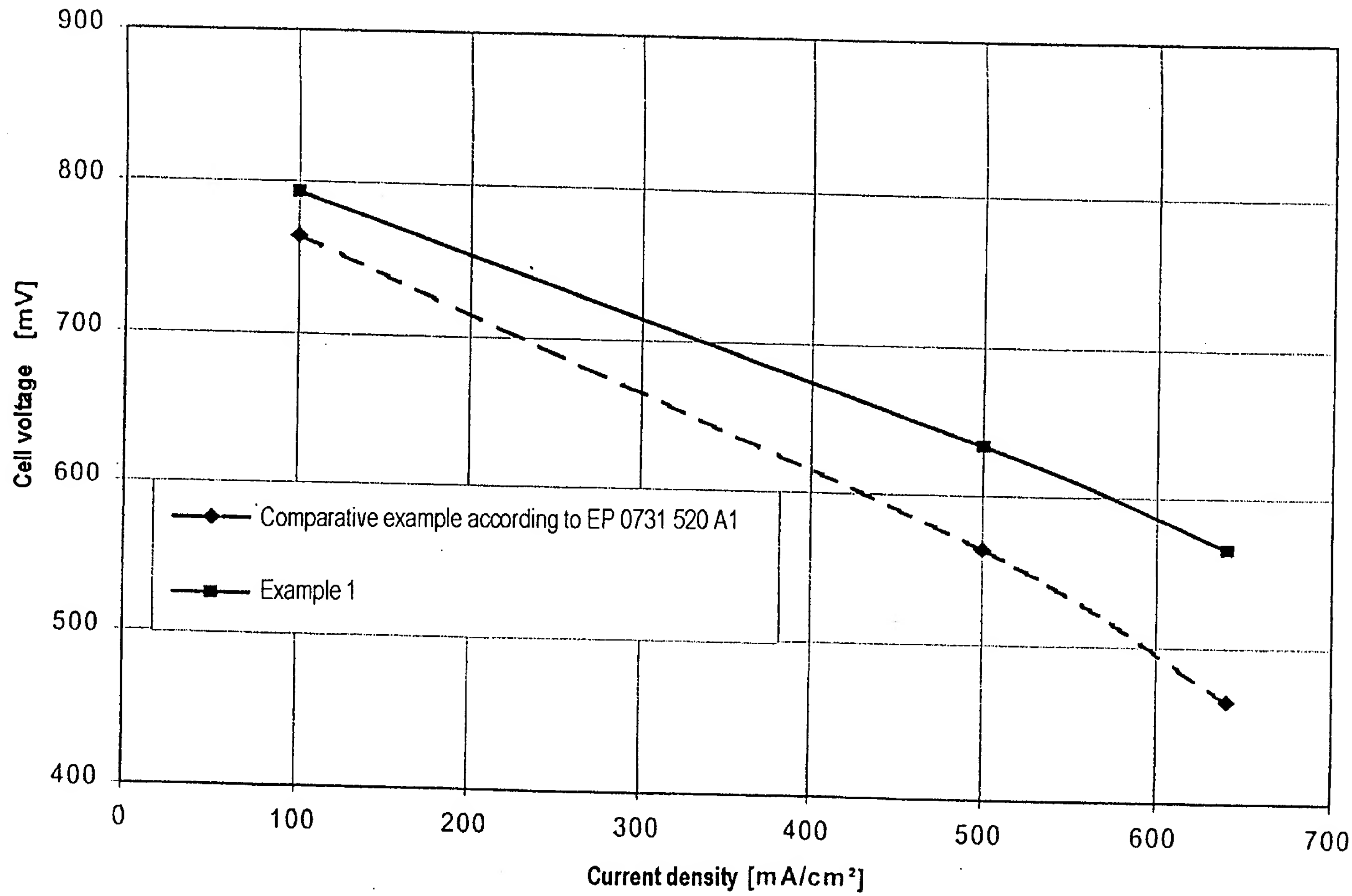
900
800
700
600
500
400
Cell voltage [mV]
0
100
200
300
400
500
600
700
Current density [mA/cm²]
Comparative example according to EP 0731 520 A1
Example 1

Figure 1